# *In Situ* Dehydration with Electrogenerated Acid and Acid Anhydride in Electrolytic Polymerization of Tetrahydrofuran

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**Abstract**

*In situ* dehydration of a trace amount of water was tried by applying an electrogenerated acid for acid-catalyzed hydrolysis of acid anhydrides added to reaction mixture as an additive. This method was very effective for the electrolytic polymerization of tetrahydrofuran with perchlorate as a supporting electrolyte.

## Introduction

Tetrahydrofuran (THF) undergoes a ring opening cationic polymerization to yield poly(oxytetramethylene) by anodic reaction with perchlorate as a supporting electrolyte.[1~5] Usually, a trace amount of water in an ionic polymerization medium reacts with initiating and propagating species to result in low yield and low molecular weight. It is necessary to use highly dry solvent for yielding the polymer with high molecular weight. However, the purification of organic solvents such as dehydration is now being carried out by tedious methods and too time-consuming procedures in many cases.

Recently, Torii et al. have developed some synthetic applications of electrogenerated acid (EGA) for acid-catalyzed reactions.[6,7] If the EGA is effective for acid-catalyzed hydrolysis of acid anhydride by the water involved in reaction mixture, it is expected that a trace amount of water can be removed *in situ* along with the progress of electrolysis by adding the acid anhydride as an additive. In this paper we describe the application of the above idea of *in situ* dehydration from the reaction mixture for the electrolytic polymerization of THF.

## Experimental

Tetrahydrofuran was purified and dehydrated by the following two methods. Method A : Distilled over $CaH_2$ after distillation over NaOH. Method B : Distilled carefully over $CaH_2$ before use after the purification by method A. Water content of the THF obtained by method B was less than the limit of detection for the coloration reaction of naphthalene and sodium. Other chemicals were dried by usual methods.

The electrolytic polymerization was carried out as follows. A 20 ml of THF

containing $LiClO_4$ (0.5 mol $dm^{-3}$) was put in anode and cathode chambers, respectively, followed by electrolysis with or without acid anhydrides under the following conditions. Anode : platinum plate (14 $cm^2$) ; Cathode : copper plate (20 $cm^2$) ; Current : 10 mA (0.71 mA $cm^{-2}$) ; Electricity passed : 144 C.

After the electrolysis, the anolyte was allowed to stand until the polymerization attained equilibrium. The yield and average molecular weight were determined as described previously.[1]

## Results and Discussion

The obtained results are summarized in Table 1. Using the THF purified by method A, the yield of polymer was very poor (run 1), but the yield and molecular weight increased extremely by using the THF purified by method B (run 2). Since the above results suggest that a trace amount of water in the reaction mixture inhibits the polymerization, the effect of acid anhydrides (maleic, succinic and phthalic anhydrides) on the yield and molecular weight were examined on the basis of the idea for dehydration by EGA-catalyzed hydrolysis of the added acid anhydrides. The tetrahydrofuran purified by method A was used in the experiments to evaluate the effect of acid anhydrides on the electrolytic polymerization.

As expected, addition of maleic anhydride increased the yield and molecular weight (runs 3 ~ 5). The same results were obtained in the cases of succinic and phthalic anhydrides (runs 6 and 7). Though the acid anhydrides are hydrolyzed to give the corresponding free acids, no influence of the formed free acids on the polymerization was observed from the

Table 1 Effect of acid anhydridries on the electrolytic polymerization of THF

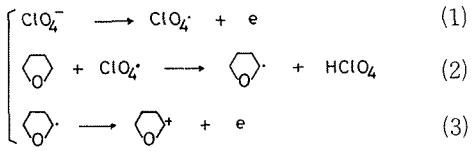
| Run | Purification of THF | Additives (molar ratio for THF) | | | | | | Yield of polymer (%) | Average molecular weight ($\times 10^{-4}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | MAH | SAH | PAH | MA | SA | PA | | |
| 1 | Method A | — | — | — | — | — | — | 6.7 | 0.84 |
| 2 | Method B | — | — | — | — | — | — | 73 | 2.31 |
| 3 | Method A | 0.01 | — | — | — | — | — | 74 | 2.91 |
| 4 | 〃 | 0.05 | — | — | — | — | — | 70 | 3.20 |
| 5 | 〃 | 0.10 | — | — | — | — | — | 73 | 2.81 |
| 6 | 〃 | — | 0.10 | — | — | — | — | 70 | 3.04 |
| 7 | 〃 | — | — | 0.05 | — | — | — | 73 | 3.27 |
| 8 | 〃 | 0.10 | — | — | 0.01 | — | — | 75 | 3.23 |
| 9 | 〃 | — | 0.10 | — | — | 0.01 | — | 75 | 3.17 |
| 10 | 〃 | — | — | 0.05 | — | — | 0.005 | 65 | 3.22 |
| 11 | 〃 | — | — | — | 0.01 | — | — | trace | — |
| 12 | 〃 | — | — | — | — | 0.01 | — | trace | — |
| 13 | 〃 | — | — | — | — | — | 0.01 | trace | — |

MAH : Maleic anhydride, SAH : Succinic anhydride, PAH : Phthalic anhydride
MA : Maleic acid, SA : Succinic acid, PA : Phthalic acid

results in the presence of both acid anhydride and the corresponding free acid (runs 8～10). However, the addition of only free acids without acid anhydrides prevented the polymerizayion to result in very low yield (runs 11～13).

The electrogenerated acid formed in anolyte is supposed to be a perchloric acid in the electrolysis with perchlorate as a supporting electrolyte and the following two reaction schemes for the initial electron transfer have been proposed by considering a discharge of perchlorate anion [5] and THF itself. [2] Since one

Scheme 1



(1)

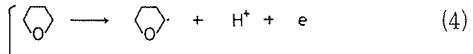


(2)

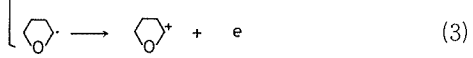


(3)

Scheme 2



(4)

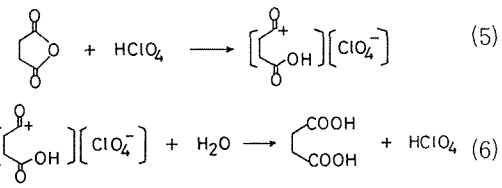


(3)

mol of the acid and $\alpha$-carbonium ion of THF is formed by two-electron transfer in any case, there is no great difference between schemes 1 and 2 for the subsequent polymerization. Furthermore, it is also reasonable to assume the formation of the $\alpha$-carbonium ion, because the methoxylation of THF at its $\alpha$-position occurs in methanol with sodium methoxide or ammonium nitrate as a supporting electrolyte. [8]

The formed perchloric acid and $\alpha$-carbonium ion of THF initiate the polymerization, and the perchloric acid as an EGA catalyzes the hydrolysis of the acid anhydride added to the polymerization medium. In fact, about 0.7m moles of perchloric acid were detected in the electrolysis of 144C as the pyridinium salt from the aqueous solution after the precipitation of the resulting polymer with water. The current efficiency was 90% as one electron reaction for the formation of the acid accordiug to the above reaction schemes.

The acid-catalyzed hydrolysis of acid anhydride proceeds as follows for an example of succinic anhydride. Though the



(5)

(6)

cation formed in eq. ( 5 ) is also expected to be an initiating species, the polymer incorpolating such species, as well as that derived from maleic and phthalic anhydrides, as an end group was not detected by infrared analysis. It is therefore considered that the cation in eq. ( 5 ) is responsible more for the subsequent hydrolysis in eq. ( 6 ) than for an initiating reaction.

When acetic anhydride was used as one of acid anhydride, acetyl cation ($CH_3\overset{+}{C}O$) formed by the corresponding reaction to eq. ( 5 ) initiated the polymerization of THF to yield dimer, trimer, oligomer and polymer with acetate in both end groups. Since this reaction exhibited some interesting behaviors by alternations in the electrolytic conditions, details will be reported compared with the chemical polymerization by acetic anhydride and perchloric acid [9] in a subsequent paper.

At any rate, the above results and discussion support the effectiveness of *in situ* dehydration in the electrolytic polymerization medium containing acid anhydrides as an additive, and such interest-

ing dehydration method can be applied for other reactions.

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